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(54) PHOTSENSITIVE PASTE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a photosensitive paste which does not cause thickening and caking, even when powder of copper, glass, ceramics or the like is used.
SOLUTION: The photosensitive paste contains an inorganic powder, at least an alkali-soluble acrylic copolymer as a photosensitive organic component and a photopolymerization initiator as essential components. The acid value of the acrylic copolymer is 50-80.

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CLAIMS

[Claim(s)]

[Claim 1]Inorganic powder and photosensitive paste characterized by an acrylic copolymer of alkali solubility, and being photosensitive paste which uses a

photopolymerization initiator as an essential ingredient, and acid values of said acrylic copolymer being 50-80 at least as a photosensitive organic component.

[Claim 2]The photosensitive paste according to claim 1, wherein acid values of an acrylic copolymer are 70-80.

[Claim 3]The photosensitive paste according to claim 1 characterized by including copper powder at least as inorganic powder.

[Claim 4]The photosensitive paste according to claim 1 characterized by including glass powder at least as inorganic powder.

[Claim 5]The photosensitive paste according to claim 1 characterized by including ceramics powder at least as inorganic powder.

[Claim 6]The photosensitive paste according to claim 1 which an acrylic copolymer makes it weight average molecular weight calculated from polystyrene reduced molecular weight by GPC, and is characterized by being 3000-20000.

[Claim 7]The photosensitive paste according to claim 1 which an acrylic copolymer makes it weight average molecular weight calculated from polystyrene reduced molecular weight by GPC, and is characterized by being 5000-12000.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the photosensitive glass paste for forming photosensitive conductive paste for forming a conductive pattern on a ceramics board or a glass substrate, and an insulating layer, a photosensitive glass ceramic paste, and photosensitive ceramic paste.

[0002]

[Description of the Prior Art]The multi chip module carried in a personal computer and a PC card in recent years, A demand of a miniaturization, densification and highly-minute-izing, and high-reliability is increasing to electronic parts or ceramic multilayer substrates, such as a filter for high frequency of mobile transmitter dexterous ways, such as a chip-size package or a cellular phone, a chip inductor, and a multilayer ceramic capacitor. The demand to the minuteness making of an electrode is also increasing with highly-minute-izing of displays, such as a plasma display. Various kinds of detailed conductor film formation methods are proposed to these demands.

[0003]Typical methods include a film method, plating, and thick film printing. After a film method forms membranes by weld slag, vacuum evaporation, etc., although resolution last shipment=20 / patterning of not less than 20 micrometers is possible for it, with photolithography technology, By this method, the thickness of a conductor film is proportional to weld slag or the process time of vacuum evaporation, since it has a long time in order to thicken, only a thin film is obtained, but there is a fault that as a result the impedance as a circuit becomes high. In plating, there is a problem that formation of thick-film elements, such as a resistor, is difficult in a baking process.

[0004]On the other hand, although it is easy to thicken a conductor film or to carry out the simultaneously form of the passive components, such as a resistor, in the thick film printing formed by screen-stencil, On the other hand, there was a problem that line formation of constant width is difficult, and sectional shape came on boiled fish paste, and the design of an electrical property side was difficult, in last shipment=50 / resolution of 50 micrometers or less.

[0005]When forming a multilayer interconnection layer on a ceramics board, wiring becomes detailed and the through hole which combines between the layers of an insulating layer is also asked for a detailed thing. When forming insulating layers, such as glass, a glass ceramic, and ceramics, on a ceramics board, there are thick film printing and the green sheet method, but it is difficult to form a through hole of 100 micrometers or less by any method.

[0006]There is a photosensitive paste method to improve the definition of thick film printing and sectional shape. This uses what has photosensitivity as the conductive paste for thick film screen printing, or insulating paste, and can form the thick film conductor pattern and through hole of high resolution by passing through mask exposure and the process of development after printing. Many things with which what mixed the end of conducting powder, such as metal and carbon, to the photo-setting resin mixed powder, such as glass and ceramics, to the photo-setting resin as photosensitive insulating paste as photosensitive conductive paste are used.

[0007]

[Problem(s) to be Solved by the Invention]Although the photosensitive paste method was a method outstanding in this way, the acrylic copolymer mostly used as a photopolymer reacted to a certain kind of metal, and there were a viscosity rise and a problem of solidifying when severe. The end of conducting powder did not produce the reaction, when [like gold and silver] it was the stable precious metals chemically, but this problem was remarkable when copper which is a base metal and metal very suitable as a wiring material whose electrical resistance it is especially cheap and is low was used. Many metallic oxides were contained in the ingredient of glass or ceramics, and the problem of the same thickening as beam copper and solidification might therefore already occur in the kind of this metallic oxide.

[0008]Even if powder, such as copper, or glass, ceramics, is used for the purpose of this invention, there is in supplying the photosensitive paste which neither thickening nor solidification produces.

[0009]

[Means for Solving the Problem]This invention is photosensitive paste characterized by acid values of said acrylic copolymer being 50-80 in an acrylic copolymer of alkali solubility, and photosensitive paste which uses a photopolymerization initiator as an essential ingredient at least as inorganic powder and a photosensitive organic component.

[0010]

[Embodiment of the Invention]Although this invention is explained concretely below, this invention does not receive any restriction by these explanation.

[0011]This invention controls the reactivity of the photopolymer in photosensitive paste, and inorganic powder, thickening and solidification are prevented, and stable photosensitive paste is obtained.

[0012]The acrylic copolymer of alkali solubility is a copolymer of acid monomers, such

as acrylic acid and methacrylic acid, and monomers, such as acrylate and methacrylate, and acid value is determined by the quantity of the acid monomer in a copolymer. Artificers trace that the point of reacting to metal, such as copper, is in this acid monomer by research, and by specifying acid value, the quantity of the acid monomer in an acrylic copolymer and a jam inhibit a reaction with inorganic powder, and come to complete stable photosensitive paste.

[0013]The photosensitive organic components used by this invention are polymer of alkali solubility, polyfunctional monomer which has two or more carbon-carbon double bonds in one molecule, and an organic component which bears the photosensitivity in photosensitive paste which uses a photopolymerization initiator as an essential ingredient.

[0014]An acrylic copolymer is used as polymer of alkali solubility. An acrylic copolymer is a copolymer which contains an acrylic system monomer in a copolymerization ingredient at least, and with an acrylic system monomer. As a concrete example, methyl acrylate, ethyl acrylate, n-propylacrylate, Isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, Isobutyl acrylate, tert-butyl acrylate, n-pentyl acrylate, Allyl acrylate, benzyl acrylate, butoxy ethyl acrylate, Butoxytriethylene glycol acrylate, cyclohexyl acrylate, Dicyclopentanyl acrylate, dicyclopentenylacrylate, 2-ethylhexyl acrylate, glycerol acrylate, glycidyl acrylate, Heptadecafluorodecyl acrylate, 2-hydroxyethyl acrylate, ISOBO nil acrylate, 2-hydroxypropyl acrylate, ISODEKI sill acrylate, Isooctyl acrylate, laurylacrylate, 2-methoxy ethyl acrylate, methoxy ethylene glycol acrylate, methoxy diethylene-glycol acrylate, octaphloropentyl acrylate, Phenoxy ethyl acrylate, stearylacrylate, triphloroethyl acrylate, Acrylamide, aminoethyl acrylate, phenyl acrylate, Acrylic system monomers, such as phenoxy ethyl acrylate, 1-naphthyl acrylate, 2-naphthyl acrylate, thiophenol acrylate, and benzyl mercaptan acrylate, the thing which replaced these acrylate with methacrylate, etc. are mentioned. It is alkyl acrylate or alkyl methacrylate, and that methyl methacrylate is included at least more preferably desirably, and the good polymer of pyrolysis nature can be obtained. Although it is usable as copolymerization ingredients other than an acrylic system monomer in all the compounds which have a carbon carbon double bond, Preferably Styrene, p-methylstyrene, o-methylstyrene, m-methylstyrene, Styrene, such as alpha-methylstyrene, chloromethyl styrene, and hydroxymethylstyrene, gamma-meta-KURIROSHIKI propyltrimethoxysilane, a 1-vinyl-2-pyrrolidone, etc. are mentioned.

[0015]Not the organic solvent in which a problem is in environment but an alkaline aqueous solution can be used as a developing solution because polymer has alkali solubility. In order to give alkali solubility to an acrylic copolymer, it is attained by adding unsaturated acid, such as unsaturated carboxylic acid, as a monomer. As a concrete example of unsaturated acid, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinyl acetate, or these acid anhydrides are mentioned.

[0016]As for the acid value of polymer by adding these, it is preferred that it is the range of 50-80. More desirable ranges are 70-80. If acid value is larger than 80, reactivity with copper or glass will be remarkably high, and will cause thickening and solidification of a paste. Solubility [as opposed to / that acid value is less than 50 / an alkaline aqueous solution] is low, and when developing negatives with an alkali developing solution, developing time is remarkably long or it becomes impossible to completely develop negatives.

[0017]Although the reactivity of resin and inorganic powder falls by lowering acid value, As for an acrylic copolymer, since the solubility over alkali falls and developing time becomes long, in order to reconcile the stability of a good paste, and good development nature, it is desirable for a molecular weight to be low in addition to being the acid value of the above-mentioned range. It is made the weighted mean average molecular weight calculated from the polystyrene reduced molecular weight by GPC (gel permeation chromatography) as a desirable molecular weight, is 3000-20000, and is 5000-12000 more desirably. If a molecular weight exceeds 20000, the solubility over an alkali developing solution will fall and developing time will become long. When alkali solubility is too high in a molecular weight being less than 3000 and spreading desiccation not only of a good pattern not being obtained but the paste is carried out at a substrate, stickiness will arise, and handling will become difficult.

[0018]As polyfunctional monomer, the compound which has two or more carbon-carbon double bonds is used into one molecule, and as the concrete example, Arylation cyclohexyl diacrylate, 1,4-butanediol diacrylate, 1,3-butyleneglycol diacrylate, ethylene glycol diacrylate, Diethylene glycol diacrylate, triethylene glycol diacrylate, Polyethylene-glycol diacrylate, dipentaerythritol hexaacrylate, Dipentaerythritolmonohydroxypentaacrylate, ditrimethylolpropanetetraacrylate, Glycerol diacrylate, methoxy-ized cyclohexyl diacrylate, Neopentyl glycol diacrylate, propylene glycol diacrylate, Polypropylene-glycol diacrylate, triglycerol diacrylate, Trimethylolpropane triacrylate, bisphenol A diacrylate, diacrylate of a bisphenol A-ethyleneoxide addition, diacrylate of a bisphenol A-propylene oxide addition, Or although one copy or the compound altogether replaced with the methacrylic group is mentioned in the acrylic group of the above-mentioned compound, this invention is not limited to these monomers.

[0019]Although there are carbon powder, metal powder, etc. and there are gold, silver, copper, nickel, tungsten, molybdenum, etc. as metal powder as electric conduction powder used by this invention, it is not limited to these. This invention demonstrates a big effect especially, when the powder containing copper reactant high metal or its oxide is used, but this invention is not limited to the kind of these metal. As for the mean particle diameter of electric conduction powder, it is desirable that it is the range of 2-5 micrometers. When mean particle diameter was smaller than 2 micrometers and the conducting powder end of the volume is added to resin, since powdered surface area becomes large, much light is interrupted, and the light transmission inside a paste is reduced. When larger than 5 micrometers, since the surface roughness at the time of applying becomes large and pattern accuracy and dimensional accuracy fall further, it is not desirable.

[0020]As the end of insulating powder it is used by this invention, a ferrite, cordierite, Forsterite, alumina, silica, mullite, cristobalite, Corundum (alpha alumina), zirconia, a calcium oxide, magnesium oxide, Although chrome oxide, lithium oxide, lead oxide, boron oxide, iron oxide, a zinc oxide, nickel oxide, borosilicate glass, etc. are raised and the effect is demonstrated in the end of insulating powder containing especially lead oxide and a calcium oxide, it is not limited to these.

[0021]As for the mean particle diameter in the end of insulating powder, from a viewpoint of dispersibility, it is preferred that it is 0.5-7 micrometers. If distribution in a paste falls in less than 0.5 micrometer and mean particle diameter is larger than 7

micrometers, since the dimensional accuracy of a pattern and the surface roughness of a coating film surface fall, it is not desirable. From a viewpoint of photo lithography, law with much [dispersion] light which penetrates the inside of a film few is preferred, and 1 micrometers or more are preferred in that case. When these are taken into consideration, the desirable mean particle diameter in the end of insulating powder is 1-7 micrometers.

[0022]As a photopolymerization initiator, what has sensitivity to long wavelength is preferred. Since sensitivity not only improves by using to long wavelength, but it is easy to be influenced by absorption or dispersion so that the wavelength of a beam of light becomes short, in order to make it harden to the inside of a thick film, it is preferred to have sensitivity to long wavelength. Usually, since a mercury-vapor lamp is used for exposure, it is preferred to have sensitivity to the wavelength of 436 nm which is g line of the long wavelength line spectrum of a mercury-vapor lamp. The compound initiator system which gave g line sensitivity can also be conveniently used by adding a sensitizer to the photopolymerization initiator which has sensitivity only in short wavelength.

[0023]As such an initiator, as an initiator which has sensitivity, for example on g line, 2-benzyl-2-dimethylamino 1 -(4-morpholinophenyl)- There is the butanone- 1 or bis(2,4,6-trimethyl benzoyl)-phenyl phosphine oxide, Although the initiator system etc. which make 2 and 4-diethylthio xanthone act on 2-methyl-1 [4-(methylthio) phenyl]-2-morpholinopropane 1-one as a sensitizer, and give g line sensitivity to it as an initiator which does not have sensitivity on g line are mentioned as an example, The photopolymerization initiator system which can be used for this invention is not limited to these.

[0024]When it irradiates with many beams of light in order to stiffen the inside of a film, in order to prevent the pattern near the surface spreading by the scattered light, and a pattern becoming large, it is preferred to add the ultraviolet-rays extinction agent which consists of organic dye. As for an extinction agent, in order to prevent that it becomes impossible for a beam of light to reach the inside of a thick film by absorption by an extinction agent, it is desirable to decrease an absorbance by the exposure of a beam of light. Azo and a benzophenone series as an organic system color preferably. As azo dye, for example, the Sudan blue, Sudan R, Sudan II, Sudan III There are Sudan IV, oil orange SS, oil violet, an oil yellow alumnus, etc., and as a benzophenone series color, although there are Uvinul D-50 and Uvinul MS40 and Uvinul DS49 grade, it is not limited to these.

[0025]As for addition of an ultraviolet-rays extinction agent, 0.01 to 1 % of the weight is preferred. At less than 0.01 % of the weight, the effect of stopping the pattern breadth by addition is low, if 1 % of the weight is exceeded, absorption will be too large and hardening inside a film will be barred.

[0026]The paste of this invention is obtained by mixing the above-mentioned structure uniformly, for example with kneading apparatus and dispersion devices, such as 3 roll mills and KOBORUMIRU. An example is raised and explained. After mixing an organic component uniformly thoroughly with a mixer or a stirrer, the end of conducting powder is added, and also it mixes, and preliminary distribution is performed. Then, it kneads through 3 roll mills. As for 3 roll mills, it is preferred to let it pass continuously 8 times from 2 times.

[0027]Next, although the example of formation of the electric conduction pattern using the photosensitive paste by this invention is explained, this invention is not limited to

this.

[0028] On an alumina substrate, a glass substrate, etc., by screen-stencil, a paste is applied and it dries. After heating for 1 hour and drying from several minutes at 70 °C - 100 °C. It exposes via a mask. The thing of a negative mold is used for a mask to the pattern shape for which it asks, and exposure 10--300-mJ/cm²-irradiates with a light exposure by the measurement for example, in i line (365 nm) with a high-pressure mercury-vapor lamp etc. Negatives are developed by using an alkaline aqueous solution as a developing solution after exposure. In order to prevent the remains for metal, organic alkali of an alkaline aqueous solution, such as tetramethylammonium hydroxide and ethanolamine, is preferred. Rinsing is performed after carrying out predetermined time development with a developing solution. Although immersion, a spray, a paddle, etc. can perform these development and rinsing, since high resolution is obtained and the pattern of rectangular cross section shape is obtained, spray development is preferred. The spray time of a developing solution is 200 seconds from 20 seconds, and, similarly a spray performs rinsing in 60 seconds from 10 seconds. When carrying out a spray, it is preferred from a homogeneous point of development to rotate a substrate. 100-1000 rpm of revolving speed is preferred. After rinsing, rotation is raised, and excessive water is shaken off and dried. The number of rotations at this time is 1000 to 4000 rotation. After oven etc. will remove moisture thoroughly if required, it calcinates at an electric furnace, a belt furnace, etc., and an organic component is volatilized and a conductor film or an insulator layer can be formed by making inorganic powder sinter. Although they change with kinds of a conductor or substrate, a firing environments and temperature are nitrogen atmospheres, hydrogen atmospheres, etc. containing atmospheric air, a nitrogen atmosphere, and 10-100 ppm of oxygen, at the temperature of 500-1600 °C, are held for 1 to 60 minutes, and are calcinated.

[0029] The pattern formed with the photosensitive paste of this invention, The substrate for MCM (multi chip module) mounted in a notebook computer or a cellular phone, Although the substrate for CSP (chip-size package) is begun and it is used suitably for electrodes, such as chips, such as a chip inductor and a chip capacitor, and a module board, an insulating layer and plasma address liquid crystal, the electrode for plasma display panels, a nonconductor pattern, etc., It is not limited to these uses.

[0030]

[Example] Although the following examples explain this invention concretely, this invention does not receive any restriction according to these examples. The paste was adjusted in the way described below about each presentation shown in Table 1, and pattern processing nature was examined. The used raw materials are shown below.

[0031] A. -- copper powder for inorganic powder a. conductive paste mono dispersion -- granular . mean-particle-diameter specific surface area [of 3.6 micrometers] 1.0 (m²/g) tap density Glass powder for the end of b. insulating powder with pretreatment by a 4.5 (g/cm³) (made by Dow Mining) powder maker mono dispersion -- spherical Mean particle diameter of 2.7 micrometers Specific surface area 1.91 (m²/g). glass transition point 670 °C. B. polymer glycidyl methacrylate denaturation methacrylic acid-methyl methacrylate copolymer a. acid value 74 weight average molecular weight 10000b. acid value 100 weight average molecular weight 23000c. acid value 48 weight average molecular weight . 10000d. acid value 66 weight-average-molecular-weight 23000 (in addition -- an example.) 10000e. acid value 74 weight average molecular weight 2800f.

acid value 74 weight average molecular weight 4000g. acid value 74 weight average molecular weight 15000h. acid value 74 weight average molecular weight The weight average molecular weight in a comparative example was obtained by polystyrene conversion with gel permeation chromatography (GPC).

[0032]C. Polyfunctional monomer propylene oxide denaturation trimethylolpropane triacrylate 3 organic-functions monomer Double bond equivalent 157g/mol tPA-330 (Nippon Kayaku)

D. Photoinitiator 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl)- Butanone- 1 (IRGACURE 369 of Tiba Speciality Chemicals; referred to as IC369 below)

E. Solvent gamma butyrolactone F. dispersing agent dispersing agent a:" NOPUKO sparse 092" (made by Sannopuko)

G. Extinction agent Sudan IV (Tokyo Chemicals)

H. Leveling agent LC-951 (effective concentration is 10 % of the weight, and the remainder is a solvent) (Kusumoto Chemicals)

I. Glass frit glass frit a:ZrO₂ (42), B₂O₃SiO₂ [(24)]₂(21) Li₂O(7) aluminum₂O₃ (4) and other oxides (2) Unit: % of the weight J. developing solution tetraethylammoniumhydroxide 0.1-% of the weight solution.

[0033]All the following work was done under yellow light.

A solvent is mixed with paste adjustment (1) polymer, and it heated for 3 hours and was made to dissolve at 60 **.

(2) The polymer solution was cooled to the room temperature, all other presentations were mixed, and it mixed with the motor uniformly thoroughly at the room temperature at 200 rpm for 30 minutes using churning feather.

(3) The obtained slurry was kneaded with 3 rolls (EXACT model 50), and the paste was obtained.

[0034]The pattern processing (1) paste was completely applied by screen-stencil on the 96% alumina substrate of a 7.5-cm angle (made by Nikko). A screen uses SUS#325 mesh. Conductive paste performed printing once and insulating paste performed the 2nd overprint after the temporary dryness for 10 minutes at 80 ** after the 1st printing.

(2) The printed substrate was dried at 80 ** in hot wind oven for 40 minutes. In conductive paste, the thickness after desiccation was 15 micrometers and insulating paste was 35 micrometers.

(3) The paste was exposed via the pattern mask using the high-pressure mercury-vapor lamp (15 mW/cm²). The pattern mask for conductive paste is a line/space pattern, and between line width/line used the thing of 30/30, 40/40, 50/50, 60/60, 70/70, and 80/80 (unit: micrometer), respectively. The case where O and an 80-micrometer pattern have resolved the case where O and a 50-micrometer pattern are able to resolve the case where a 30-micrometer pattern is able to be resolved was made into **, and when the resolution not more than it or development was improper, it indicated to Table 1 as x. The pattern mask for insulating paste is a through hole mask of 50 micrometerphi. When 50 micrometerphi has been resolved, it was estimated as O.

(4) Using the alkali developing solution (0.1%TMAH solution), it was immersed, and the substrate after exposure was made to rock, and was developed, and it rinsed in the water shower after that.

(5) The pattern was observed with the optical microscope.

[0035]Viscosity was measured immediately after stability test (1) paste creation.

(2) Viscosity was again measured after one-week settlement at the room temperature. All results were shown in Table 1.

[0036] Examples 1-7 are examples of the paste which used copper powder. The comparative examples 1 and 2 are examples using the polymer which has the acid value besides the range of this invention. In the comparative example 1, since [that the acid value of polymer is high] reactivity with copper is high, preservation stability is bad. In the comparative example 2, since the acid value of polymer was low, preservation stability was good, but alkali development property fell, and an exposure part and an unexposed part were not dissolved at all in the development by an alkaline aqueous solution, but development was impossible.

[0037] On the other hand, in Example 1, the paste with good preservation stability and development nature is obtained. In Example 2, preservation stability and pattern processing nature were good. However, pattern definition was a little inferior in alkali solubility a little low.

[0038] Example 3 and Example 4 are acid values equivalent to Example 1, and are a case where polymer with a low molecular weight is used. Examples 5 and 6 are examples at the time of using polymer with Example 1, equivalent acid value, and a high molecular weight. Although the preservation stability of the paste was good, alkali development property was low. Example 7 and the comparative example 3 are examples of the paste which used glass powder. The polymer b of the high acid value besides the range of this invention is used for the comparative example 3. Although Example 7 of preservation stability is good, in the comparative example 3, viscosity is increasing remarkably at one week of room temperatures.

[0039] According to this invention, the reaction of copper powder, glass powder, etc. and a photopolymer is inhibited, and it is stable, and it is clearer than the result obtained in Table 1 that photosensitive paste excellent in development nature is obtained.

[0040]

[Table 1]

[illegible]

[Effect of the Invention] In this invention, it has the above composition.

Therefore, the reactivity of the photopolymer in photosensitive paste and inorganic powder is controlled, thickening and solidification are prevented effectively, and stable photosensitive paste can be obtained.

[Translation done.]